

BIBLIOGRAPHIC DATA SHEET		1. Report No. APTD-1130	2. PB 210 679
4. Title and Subtitle National Inventory of Sources and Emissions Barium, Boron, Copper, Selenium, and Zinc 1969 - Selenium Section IV		5. Report Date April 1972	
7. Author(s) W. E. Davis		6.	
9. Performing Organization Name and Address W. E. Davis & Associates 9726 Sagamore Road Leawood, Kansas		8. Performing Organization Rept. No.	
		10. Project/Task/Work Unit No.	
		11. Contract/Grant No. 68-02-0100	
12. Sponsoring Organization Name and Address ENVIRONMENTAL PROTECTION AGENCY Office of Air Programs Research Triangle Park, North Carolina		13. Type of Report & Period Covered	
		14.	
15. Supplementary Notes			
16. Abstracts Information is provided regarding the nature, magnitude, and extent of the emissions of selenium in the United States for the year 1969. Background information concerning the basic characteristics of the selenium industry has been assembled and included. Brief descriptions are given; they are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant. The selenium emissions and emission factors are based on data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations. Emissions to the atmosphere during the year were 986 tons. The emissions that resulted from the combustion of coal were about 65 percent of total emissions, and those due to the manufacture of glass were nearly 21 percent. Emissions from metallurgical processing of nonferrous metals and the burning of fuel oil were 9 percent and 7 percent respectively, while all other emissions were less than one percent of the total.			
17. Key Words and Document Analysis. 17a. Descriptors Air pollution Selenium inorganic compounds Inventories Exhaust emissions Industrial wastes Coal Glass Metal industry Fuel oils			
17b. Identifiers/Open-Ended Terms			
17c. COSATI Field/Group 13B		Reproduced by NATIONAL TECHNICAL INFORMATION SERVICE U.S. Department of Commerce Springfield VA 22151	
18. Availability Statement Unlimited		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 57
		20. Security Class (This Page) UNCLASSIFIED	22. Price \$4.50

APD - 1130

REPORT

NATIONAL INVENTORY OF SOURCES AND EMISSIONS
BARIUM, BORON, COPPER, SELENIUM, AND ZINC

1969

for

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF AIR PROGRAMS
CONTRACT NO. 68-02-0100

SELENIUM

SECTION IV

by

W. E. Davis

W. E. Davis & Associates
9726 Sagamore Road
Leawood, Kansas

April 1972

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PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. 68-02-0100 with the Environmental Protection Agency, Office of Air Programs.

The inventory of atmospheric emissions has been prepared to provide reliable information, regarding the nature, magnitude, and extent of the emissions of selenium in the United States for the year 1969.

Background information concerning the basic characteristics of the selenium industry has been assembled and included.

Process descriptions are given; but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact all of the primary producers and about twenty percent of the companies in each major emission source group to obtain the required information. It was known that published data concerning emissions of the pollutant were virtually nonexistent, and contacts with industry ascertained that atmospheric emissions were not a matter of record. The selenium emissions and emission

factors ~~that are~~ presented are based on the summation of data obtained from production and reprocessing companies. Additional information was acquired during field trips to inspect the air pollution control equipment and observe processing operations.

ACKNOWLEDGEMENTS

This was an industry oriented study and the authors express their appreciation to the many companies and individuals in the selenium industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal and State Governments.

Our express thanks to Mr. C. V. Spangler, Project Officer, EPA, Office of Air Programs, Research Triangle Park, N. C., for his helpful guidance.

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SUMMARY

The production and use of selenium in the United States has been traced and charted for the year 1969. The consumption was 728 tons, while primary and secondary production was only 630 tons. Imports, principally from Canada, totaled 273 tons.

Emissions to the atmosphere during the year were 986 tons. The emissions that resulted from the combustion of coal were about 65 percent of total emissions, and those due to the manufacture of glass were nearly 21 percent. Emissions from metallurgical processing of nonferrous metals and the burning of fuel oil were 9 percent and 7 percent respectively, while all other emissions were less than one percent of the total.

Emission estimates for the manufacture of glass and metallurgical processing are based solely on data obtained from industry. Emissions due to the combustion of coal and fuel oil are based on the analytical results obtained from relatively few samples.

TABLE I
EMISSIONS BY SOURCE
1969

<u>Source Category</u>	<u>Source Group</u>	<u>Emissions - Tons</u>	<u>Emissions %</u>
Mining and Milling	N		
Metallurgical Processing	85		8.6
Secondary Production	1		0.1
End Product Uses	204		20.7
	Electronic and Electrical Glass	N 203	
	Duplicating Machines Pigments	N 1	
	Miscellaneous	N	
Other Emission Sources	696		70.6
	Coal	630	
	Oil	65	
	Incineration	1	
TOTAL	986		100.0

N - Negligible

TABLE II
EMISSIONS BY REGIONS

	<u>Tons</u>
Region No. 1	77
Region No. 2	449
Region No. 3	220
Region No. 4	<u>240</u>
TOTAL	986

<u>Region No. 1</u>		
Arizona	Montana	Utah
California	Nevada	Washington
Colorado	New Mexico	Wyoming
Idaho	Oregon	

<u>Region No. 2</u>		
Illinois	Michigan	North Dakota
Indiana	Minnesota	Ohio
Iowa	Missouri	South Dakota
Kansas	Nebraska	Wisconsin

<u>Region No. 3</u>		
Alabama	Louisiana	Tennessee
Arkansas	Maryland	Texas
Delaware	Mississippi	Virginia
Florida	North Carolina	West Virginia
Georgia	Oklahoma	District of
Kentucky	South Carolina	Columbia

<u>Region No. 4</u>		
Connecticut	New Hampshire	Pennsylvania
Maine	New Jersey	Rhode Island
Massachusetts	New York	Vermont

EMISSION FACTORS

The emission factors presented herein are the best currently available. They were determined through a combination of methods consisting of: (1) direct observation of emission data, and other related plant processing and engineering data where available; (2) estimates based on information obtained from literature, plant operators, and others knowledgeable in the field; (3) calculations based on experience and personal knowledge of metallurgical processing operations; and, (4) specific analytical results (in the case of coal and oil) where available.

The basic data used to calculate the emission factors are contained in the files of the Contractor. Readers of this document are encouraged to submit data to the EPA in confirmation of these factors, or additional data which can be used to further refine the factors in subsequent publications.

TABLE III
EMISSION FACTORS

Mining and Milling	2 lb/million tons of copper ore mined
Metallurgical Processing	277 lb/ton of selenium produced
Secondary Production	100 lb/ton of selenium recovered
End Product Uses	
Glass	2.8 lb/1,000 sq. ft. of colored structural plate glass
Pigments	15 lb/ton of selenium processed
Other Emission Sources	
Coal	2.5 lb/1,000 tons of coal burned
Oil	0.21 lb/1,000 bbls of oil burned
Incineration	20 lb/million tons of refuse burned

MINERAL SOURCES OF SELENIUM

Selenium (Se) is a relatively rare element that is widely distributed in nature. Usually it is a minor constituent of the sulfide minerals of copper, iron, and lead. Occasionally it is found in conjunction with native sulfur and in the form of selenides of other metals. The principal ores are chalcocopyrite, bornite, and pyrite.

Selenium is estimated to be the sixty-ninth most abundant element in the earth's crust at an average content of 0.09 ppm.

Copper ores are the major sources of domestic and world supplies of selenium. More than 90 percent of the domestic output of selenium, and more than 80 percent of the world's output, is as a by-product of copper refining. In the United States selenium occurs in most of the porphyry copper deposits in the western mining areas. In Canada considerable quantities are found in copper-nickel ores in Ontario, in copper-zinc ores in Manitoba, and in copper ores in Quebec. Mexico's reserves are generally associated with lead ores. The large reserves in other countries are usually found in copper ores.

Most of the selenium is recovered from the material referred to as anode mud or slime, which occurs during the electrolytic refining of copper. About 150 to 200 tons of copper ore are required in order to produce one pound of selenium.

MATERIAL FLOW THROUGH THE ECONOMY

The sources and uses of selenium in the United States during 1969 are shown in Figure I. The U. S. consumption, which totaled 728 tons, was from primary production (62 percent), secondary production (1.5 percent), imports (27.5 percent), and industry stocks (9 percent). Approximately 265 tons were exported.

The most important application of selenium during 1969 was in glassmaking. About 31 percent was used as a decolorizer, and also as a colorant in flat glass, pressed glass, and blown glass. The second largest quantity was for duplicating machines. Approximately 22 percent was used in xerography to coat the metal cylinders from which the photographic image is transferred by static electricity. Other uses included electronic and electrical equipment (16 percent), pigments (14 percent), and miscellaneous applications (17 percent).

SELENIUM
MATERIAL FLOW THROUGH THE ECONOMY - 1969
(Short Tons - Se Content)

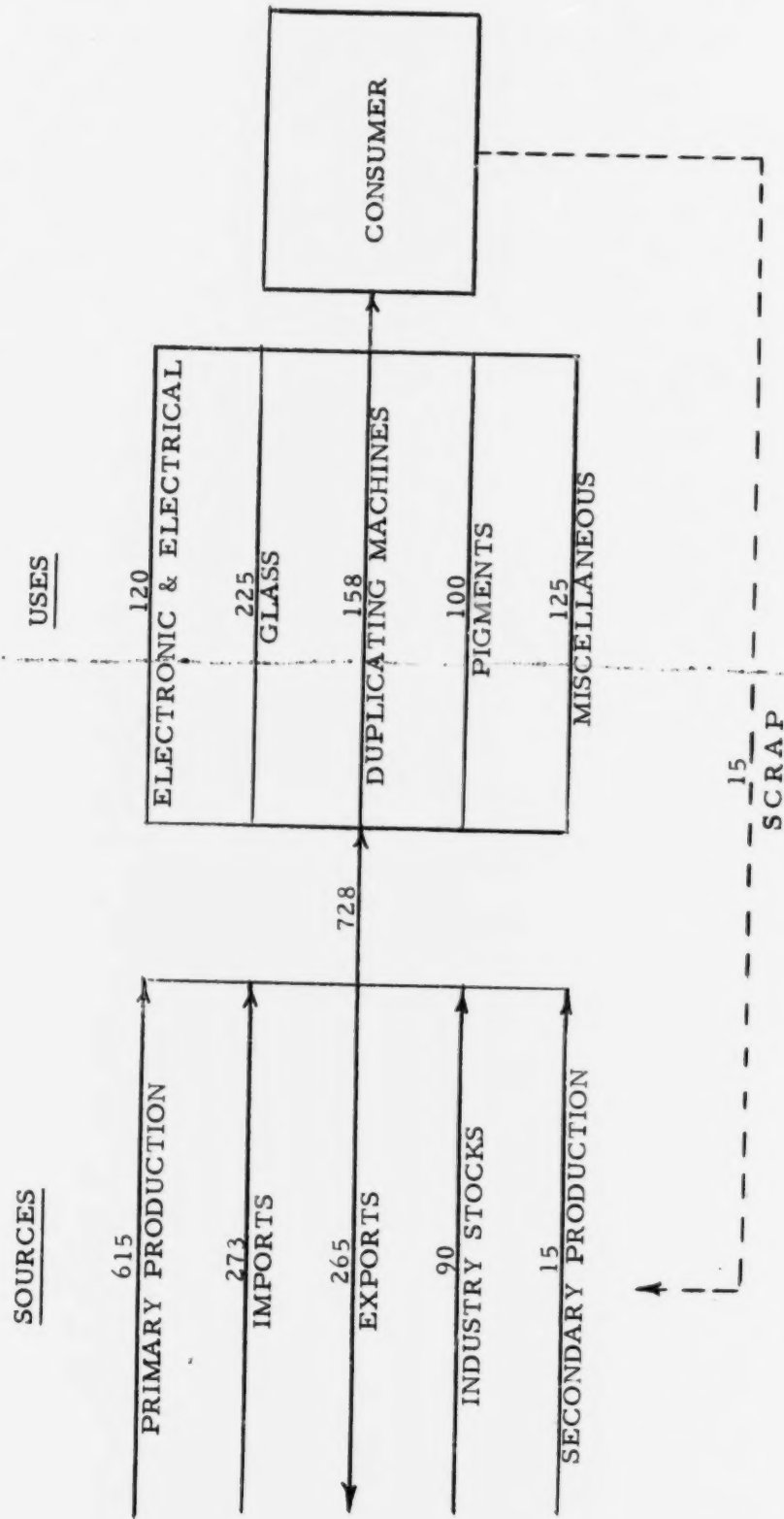


Figure 1

USES AND EMISSIONS OF SELENIUM

MINING AND MILLING

Since selenium recovery in the United States is principally as a by-product of copper refining, the selenium emissions to the atmosphere that result from mining operations are closely related to emissions that occur during the mining and milling of copper-bearing ores.

Regardless of the type of mine (underground or open-pit), the first steps in processing sulfide and non-sulfide ores are basically the same: ore removal, ore handling, crushing, and grinding. The ore is dry or sometimes damp when removed from the mine and while crushing, but is wet during the grinding step.

Emissions from Mining and Milling - While this study was in progress, 23 of the 25 leading copper-producing mines in the United States were contacted concerning the quantity of ore mined, its selenium content, and the selenium emissions that occur during mining and milling. The information obtained from 6 companies concerning 15 mining operations indicates there are slight emissions due to handling, crushing, and as a wind loss from tailings.

During 1969 there were 223,752,000 tons of copper ore produced in the United States 1/ containing approximately 2,500 tons of selenium. The selenium emissions to the atmosphere from sources of mining and milling are estimated by the Contractor at 2 pounds per million tons of copper mined, or nearly 450 pounds for the year 1969.

1- Minerals Yearbook, Bureau of Mines; 1969.

METALLURGICAL PROCESSING

In the United States primary selenium is produced at the following major electrolytic copper refineries: American Metal Climax, Inc., Carteret, New Jersey; American Smelting and Refining Company, Baltimore, Maryland; International Smelting and Refining Company, Perth Amboy, New Jersey; Kennecott Copper Corporation, Garfield, Utah; and Kennecott Refining Corporation, Ann Arundel County, Maryland. It is recovered principally from the anode slimes generated by electrolytic copper refining operations.

In order to identify the sources of emissions to the atmosphere during the recovery of selenium, it is necessary to start with the copper ore, then trace the selenium through copper smelting, electrolytic copper refining, and precious metal recovery. There are many components in the ore that must be separated in a relatively pure state. These may include copper, lead, arsenic, bismuth, antimony, gold, silver, selenium, tellurium, and platinum group metals. The operations required to carry out these separations are complex and treatment flow diagrams are complicated.

Concentration of copper ores may be accomplished by flotation

or hydrometallurgy. Flotation is the principal method used for copper sulfide ores, which comprise the bulk of copper ore production in the United States. Hydrometallurgy is used for oxide ores since they cannot be effectively concentrated by flotation.

Current copper smelting practices in the United States are similar with respect to the major operations. As shown in Figure II, the ores and concentrates first enter the roaster for removal of part of the sulfur. The calcine from the roaster is charged to the reverberatory furnace where copper matte is produced. The matte, usually containing less than 50 percent copper, is sent to the converter. Blister copper from the converter contains about 99 percent copper with the remaining one percent consisting of other metals, oxygen, and sulfur.

To refine the blister copper two steps are usually employed: fire refining, followed by electrolytic refining. Fire refining is primarily for the purpose of eliminating most of the remaining sulfur dioxide from the metal after which the resulting product is cast into anodes for the electrolytic process. During electrolysis the anodes are corroded and the copper is deposited on the cathode. The selenium and

COPPER SMELTER FLOW DIAGRAM

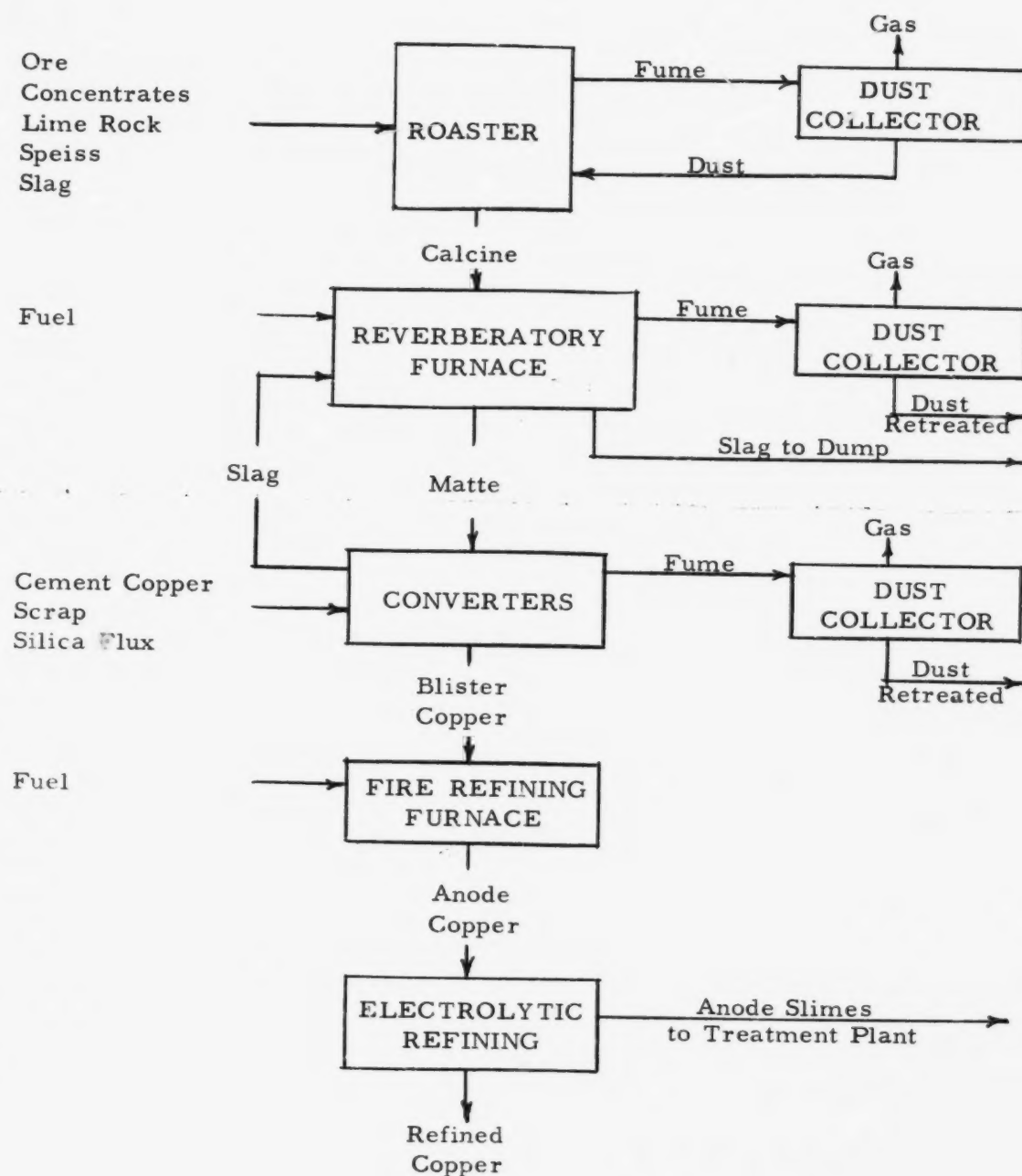


Figure II

other metals in the anode collect in the slimes that are formed during the process. Often the other metals are the most important constituents in the slimes and more emphasis is placed on their recovery than on the recovery of selenium. The primary purpose of slimes treatment is the recovery of precious metals.

Practices followed for treatment of slimes vary greatly among the refineries due to the variation in composition of the ore smelted to copper anodes and the resulting variation in the composition of the slimes. The range of slimes composition is wide, but typical values are as follows: copper, 11 to 67 percent; silver plus gold, one to 32 percent; selenium, 3 to 28 percent; tellurium, from a trace to 8 percent; lead, up to 24 percent; and arsenic plus antimony plus bismuth, up to 14 percent.

The most important methods practiced for recovering selenium from slimes are: (1) soda smelting; (2) soda roasting; and, (3) sulfuric acid roasting. All have been used successfully; however, soda roasting is not feasible with high-tellurium slimes when recovery of high-purity selenium is desirable. From the standpoint of atmospheric emissions, there appears to be no appreciable difference between the

various treatment methods. The degree of emissions seems to be more dependent on the type of equipment employed, its arrangement, and its maintenance.

The arrangement of the equipment used at one refinery for the recovery of precious metals and selenium (see Figure III) includes one furnace for drying the raw slime and a second furnace for the sulfuric acid roast. Next, water is used for leaching, then sodium hydroxide is added before the slime is ready to be placed in a small reverberatory (Doré) furnace. One scrubber and electrostatic precipitator system receives fumes from the sulfuric acid roasting furnace and a similar arrangement is provided for gases from the Doré furnace. Solutions from the scrubbers and fumes collected in the precipitators are directed to the selenium purification plant shown in Figure IV.

During purification selenium is precipitated from solutions using sulfur dioxide, then it is recovered as a crude product and combined with crude selenium from the electrostatic precipitators. The combined material is washed, dried, and distilled in a retort with the fumes being condensed to produce refined metallic selenium.

SILVER REFINERY FLOW DIAGRAM

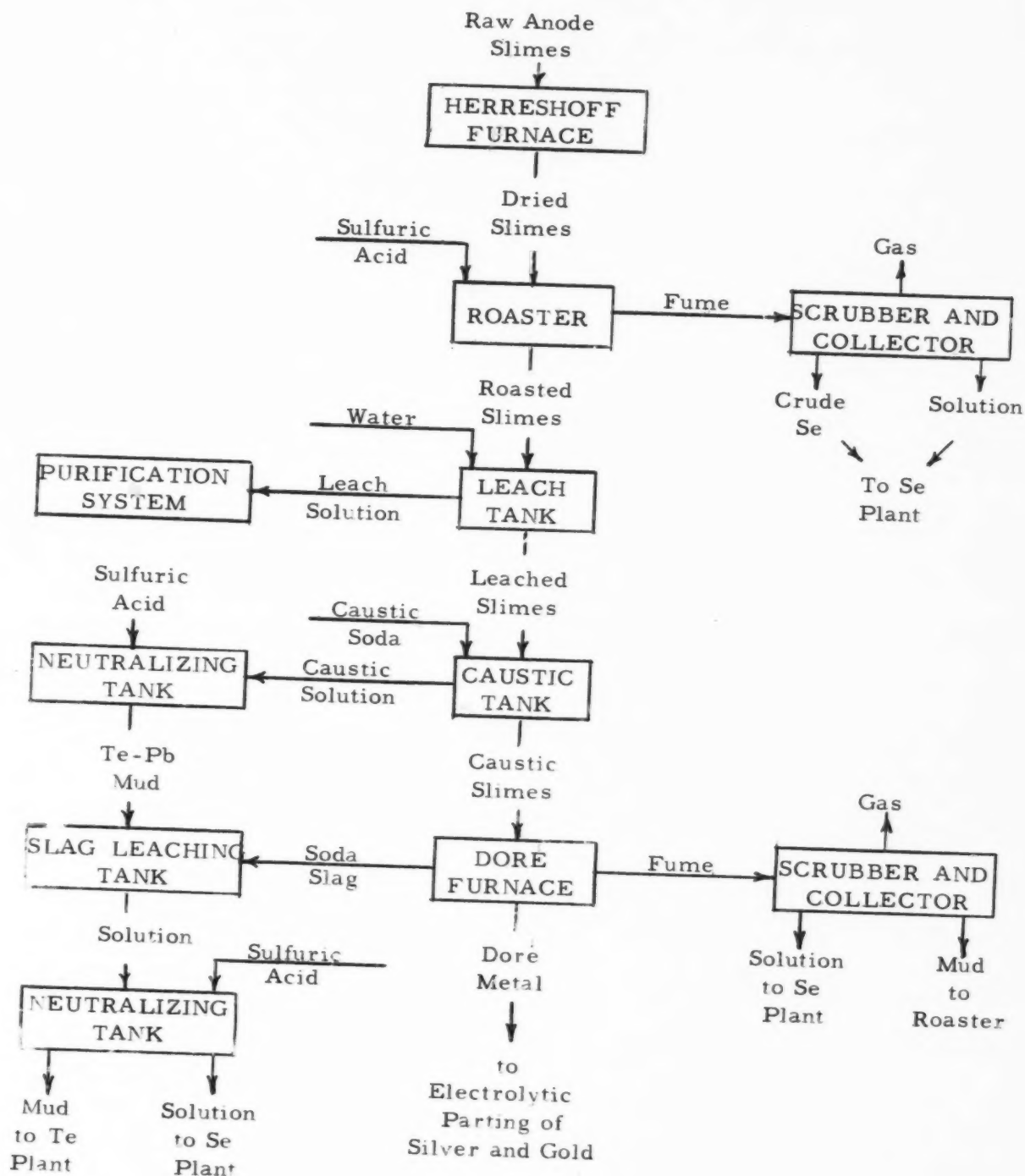


Figure III

SELENIUM PLANT FLOW DIAGRAM

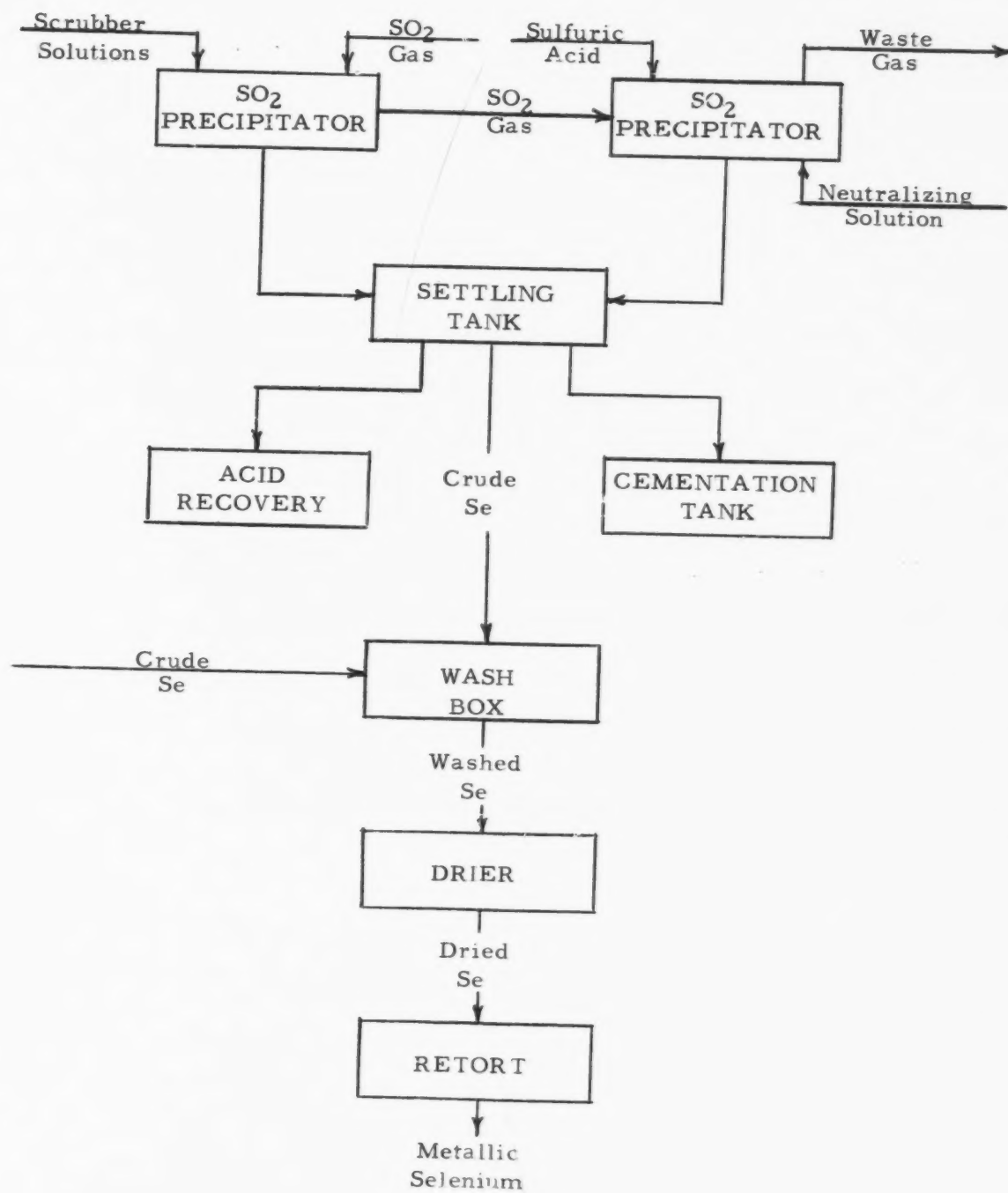


Figure IV

Throughout processing from the ore to the final product there are fumes, dusts, slags, and residues containing selenium that are discharged from dryers, roasters, furnaces, converters, and other equipment. In most cases these selenium-containing materials are collected, retreated, and recycled. At one smelting and refining complex where copper, lead, and zinc ores are processed there are several locations where fume is recycled. For example, fume from the copper roaster enters an electrostatic precipitator and the dust collected is returned to the roaster. The recycling is continuous, except periodically the dust may be directed elsewhere for recovery of certain materials that build up in the system. Fume from the reverberatory furnace also enters an electrostatic precipitator; dust collected is forwarded to a dust roaster and on to the lead processing circuit. Fume from the lead blast furnace is directed to another electrostatic precipitator and the resulting dust is returned to the lead circuit. Speiss from the lead blast furnace is directed to the copper roaster.

These are only a few of the numerous recycles and interchanges between the copper, lead, and zinc circuits. There is also recycling from precious metals recovery to the lead recovery circuit. The flow of selenium at various points in

a smelter circuit is shown in Table IV to indicate the large quantities of selenium that are recycled during the production of refined zinc, refined lead, and blister copper.

The flow of selenium in a precious metals recovery plant is shown in Table V. The recovery of selenium from slimes is indicated to be about 28 percent; however, it has been reported that higher recoveries are possible, ranging up to 80 percent 1/.

Emissions from Metallurgical Processing - During this study all of the smelting and refining companies were contacted about their selenium emissions to the atmosphere. Some information was available from 3 firms regarding overall losses, but there were only 2 sources of reliable information concerning losses to the atmosphere.

Based on data obtained from 2 sources regarding metallurgical processing of selenium-bearing ores and the production of commercial selenium, the emissions to the atmosphere during processing are 277 pounds per ton of selenium produced.

1- Kirk, R. E. and Othmer, D. F.; Encyclopedia of Chemical Technology; 2nd ed.; Interscience Publishers; New York, N. Y.; 1963.

During 1969 selenium emissions to the atmosphere in the United States resulting from metallurgical processing totaled 85 tons.

TABLE IV
SELENIUM IN INTERMEDIATE PRODUCTS
OF A SMELTER CIRCUIT

	<u>Selenium 1,000 lbs.</u>
Input to Copper Circuit	47
Input to Lead Circuit	34
Recycle from Precious Metals Plant to Lead Circuit	5
Roaster Dust to Lead Circuit	46
Sinter Flue Dust	40
Lead Furnace Flue Dust	9
Lead Furnace Slag	6
Copper Dross	32
Lead Anodes	4
Lead Fume to Cadmium Plant	2
Arsenic Roaster Calcine	40
Arsenic Precipitator Dust	41
Arsenic Produced	1
Copper Reverberatory Flue Dust	15
Copper Reverberatory Slag	6
Copper Converter Flue Dust	21
Copper Anodes	52
Blister Copper Shipped	20

Source - Private communication.

TABLE V
SELENIUM BALANCE IN ANODE RESIDUE PLANT
AND
SELENIUM-TELLURIUM PLANT

	<u>Selenium 1,000 lbs.</u>
Input in Copper Slimes	52
Input in Lead Slimes	2
Recycle to Lead Circuit	5
Output to Antimony Plant	1
Unidentified Losses in Anode Residue Plant	23
Unidentified Losses in Selenium Plant	10
Selenium Produced	15

Source - Private communication.

SELENIUM SECONDARY PRODUCTION

Secondary selenium is reclaimed principally from used xerographic copying cylinders and scrap generated during the manufacture of selenium rectifiers. It can be recovered from burned-out rectifiers, spent catalysts, and other scrap sources, but applications in chemicals, lubricating oils, pesticides, glass, and pigments normally are dissipative.

Selenium-coated metal cylinders are employed in xerography, a dry copying process. About 4 pounds of selenium are required per 100 square feet of cylinder surface, and replacement of the selenium unit may be necessary after reproducing 30,000 to 500,000 copies. The usual practice is to remove the worn-out cylinder from the copying machine and return it to the factory for reconditioning.

Emissions from Secondary Production - The industrial sources contacted during this study have indicated that small atmospheric losses occur during the recovery of secondary selenium; however, there are no test data available. Based on a description of processing operations, the Contractor has estimated emissions to be not more than 100 pounds per ton of selenium processed. In the United States the selenium emissions to the atmosphere during 1969 totaled 1,500 pounds.

END PRODUCT USES OF SELENIUM

There are satisfactory substitutes for selenium in many of its applications and its use for various purposes has varied from year to year. Sulfur and tellurium can be used as substitutes in the chemical, rubber, and steel industries. Zinc oxide and certain organic materials can serve as photoconductors in copying machines. Germanium and silicon can be utilized for rectifiers. Other important applications of selenium are found in the manufacture of glass and pigments.

Since the use of selenium can vary appreciably from year to year, emissions to the atmosphere from various sources can also vary substantially.

Electronic and Electrical Equipment - Manufacturers of electric power distribution equipment, specialty electrical transformers, rectifiers, and semiconductors have been major users of selenium metal in recent years. Together they accounted for about 16 percent of the 1969 demand. Over 90 percent of this amount was used in the manufacture of dry plate metal rectifiers.

Gray, crystalline selenium is a poor electrical conductor in the dark, but upon illumination its conductivity increases

about 3 times. Thus, selenium is used in photocells for photographic exposure meters, detectors, electric eyes, colorimeters, and pyrometers. The most efficient cells are the barrier-layer photocells in which a layer of gray selenium is supported on one side by a metal plate, usually steel or aluminum, and coated on the other side with a translucent film of gold or another metal. This film is applied by vacuum evaporation, by sputtering, or by spraying. Electrodes are then connected to the support strip and the metal film. The selenium is annealed to just below its melting point, and aged to develop sensitivity to light.

Of more importance, gray selenium is used in metal rectifiers which are similar in construction to the photoelectric cell. The rectifier consists of a layer of selenium sandwiched between a base plate and a counter electrode. The rectifying action occurs between the selenium layer and the counter electrode. During the process of manufacturing rectifiers the metal base plate is prepared and a layer of selenium is applied. Although several processes can be used, vacuum deposition of the selenium is the method currently preferred by the manufacturers contacted during this study.

Whatever the application method, the plates are heated to

just below the melting point of selenium to convert it to its gray crystalline form in order to make it a better conductor of electricity. This conversion procedure is followed by various treatments and process steps to improve properties and finish the product.

The chief merit of the selenium metal plate rectifier is in its simplicity and high efficiency. It is space saving, has a long normal life, can withstand short periods of overloading, and is suitable for rough treatment during normal operating conditions. Even though silicon and germanium rectifiers have been developed as replacements for selenium rectifiers, the development of selenium thin film devices has increased selenium usage in the power rectifier field. A disadvantage of selenium rectifiers is the proportion of defective disks manufactured. Even with the best manufacturing techniques, about 10 to 15 percent of the total production is lost. About 70 percent of the selenium consumed is deposited on the product during the vacuum plating process and most of the remainder is deposited inside the vacuum vessel.

An emission factor of 2 pounds per ton of selenium processed is estimated as the average emission rate during the manufacture of electronic and electrical equipment. The total

emissions to the atmosphere during 1969 were 240 pounds. This emission estimate was made by the Contractor on the basis of information supplied by the manufacturers.

Glass - Selenium finds two contrasting uses in the glass industry. One use is for the removal of undesirable tinges in ordinary clear glass, and the other is in the manufacture of colored glasses. Elemental selenium is generally used in glassmaking although sodium selenate, barium selenite, and sodium selenite have found some use. In decolorizing glass the selenium is added to neutralize green tints due to an iron impurity. This permits the manufacture of a clear glass.

A desirable pink tinge can be given to glass produced for food containers by using more selenium than necessary to neutralize the iron. Selenium added in larger amounts to the glass melt yields ruby-red glass for tableware, vehicular taillights, traffic and signal lens, and infrared equipment. Colored plate glass used as an outer covering material in modern office buildings also contains selenium.

Currently the glassmaking industry is the largest single user of selenium in the United States, the estimated consumption by this industry being 150 tons of selenium for the year 1969.

Raw materials for glass manufacture are shipped in packages or in bulk. Unloading may be accomplished by manual labor, vibrator-gravity, drag shovels, or vacuum systems. Methods of material storage vary widely, but in a large installation the raw materials for the glass mix are often stored in gravity feed storage hoppers and are fed directly to the weighing and mixing room. Minor ingredients are usually stored in their original containers. Cullet (waste glass or rejected ware to be remelted) must be transported to an area where the glass is segregated by type.

Glass batch mixing systems range from full automation to hand operations. Most mixers are of the rotating-barrel type which tumble the batch upon itself in a revolving drum. During a batch mixing process the materials are dry or nearly dry, which causes a loss by dusting. The glass furnace charging may be done manually or automatically, and continuously or intermittently.

Basically, the manufacture of glass is a high-temperature conversion of raw materials into a homogeneous melt for fabrication into useful articles.

There are 3 types of melting units used in the glass industry.

Clay "pots" which may be open or covered are used where quantities or special compositions do not justify the use of a tank. This process involves a relatively high proportion of manual handling. The day tank melts batches up to several tons. Finally, most glass is melted in large, direct-fired, regenerative type furnaces.

Following melting there are several ways to accomplish the forming of glass. The container industry generally is based on modifications of the blowing technique. Glass also may be pressed, cast, rolled, or drawn. Glass fibers can be made continuously by mechanical drawing, and a glass to be pulverized is dribbled or ladled into water to produce "dry gage" glass.

Final glass operations include finishing and secondary forming operations. Finishing operations may include any one or combinations of the following: flame cut-off, sawing, score and break, score-thermal crack off, thermal crack off, drilling, grinding, polishing, engraving, acid etching, glazing, and sealing. Secondary forming operations may then be used to produce difficult shapes. Before the glass becomes a finished product, a final treatment of tempering or staining may be required.

At one location where large quantities of colored structural plate glass are produced the stack effluent has been analyzed. A large part of the metallic selenium used in the batch composition is volatilized during melting. Stack effluent analysis shows that most of it is present as the red, amorphous, selenium metal. The particle size is reported to be less than 0.35 micron.

Based upon estimates obtained from the glass industry, emissions to the atmosphere resulting from the production of colored structural plate glass average 2.8 pounds per thousand square feet of glass. During 1969 selenium emissions from the glass industry totaled 203 tons.

Duplicating Machines - Amorphous selenium, a super-cooled state of liquid selenium, has found extensive use in the field of xerography since low electrical conductivity is essential. The low conductivity of selenium permits the development step to be carried out before the electrostatic image is destroyed by electrical conduction through the plate. Selenium also has good photoresponse (the electrical current resulting from illumination). It is this photocurrent which selectively discharges the xerographic plate to form an image.

The manufacture of selenium plates and drums is generally of a single basic design. The substrate is made of meticulously cleaned, oxidized aluminum, either in sheet or drum form, onto which high purity amorphous selenium is vacuum plated. Overcoating of the selenium surface is desirable to extend the xerographic plate life, but it is not generally done. During the photoreceptor manufacture, the most important variables to watch are the temperature of the substrate and the coating rate during the selenium deposition in the vacuum.

The xerographic process includes 6 steps: charging, exposure, image development, image transfer, image fixing, and photoreceptor cleaning. First, a corona charging bar sprays a positive charge on the selenium film. Next, the exposure is made so that the photoreceptor areas corresponding to the white areas of the original document are irradiated. After this electrostatic image is formed, a negatively charged, pigmented, thermoplastic powder called a "toner" is cascaded over the selenium surface. The toner adheres only to the positively charged areas. Image development continues until the positive surface charge is neutralized by the negative toner. Then, transfer of the toner to paper is done electrostatically. The paper is placed over the powder

image and the back of the paper is charged positively. Most of the toner is transferred to the paper where it is subsequently "fixed" by the addition of heat.

The principal release of selenium to the atmosphere during the manufacture of xerographic equipment occurs in connection with the vacuum plating operation. Information obtained from industry indicates that selenium emissions to the atmosphere during vacuum plating average 2 pounds per ton of selenium processed.

During 1969 selenium emissions to the atmosphere resulting from the manufacture of duplicating machines totaled 316 pounds.

Pigments - Cadmium sulfoselenide accounts for nearly all the selenium used in pigments. During 1969 this was about 14 percent of the total selenium demand. In color, the pigments vary from yellow through orange and red to deep maroon. They have considerable light stability, resistance to heat, and are not affected by sulfur gases. Originally these pigments were developed for use in ceramics, paints, enamels, and ink, but their current importance is in the plastics industry, especially in those plastics cured at high temperatures.

The most popular method for preparing these pigments is the precipitation of cadmium sulfate with a mixed solution of sodium sulfide and sodium selenide. This yellow precipitate is then washed and dried. A red color can be developed by heating the precipitate.

Cadmium-selenium pigments used in plastics are either incorporated directly into the molding powder or made into a paste and dispersed in the liquid monomer. The manufacturers of polyvinyl chloride are probably the single largest users of cadmium-selenium pigments in plastics. These pigments are used in leather cloth for cars, tablecloths, shoes, handbags, and curtains. These articles all require the use of pigments with light and heat stability. In paints, selenium pigments are used where heat treatment is required during processing. They are also used in vitreous enamels. The pigments are dispersed in liquid media, applied by painting, spraying, screen printing, or dipping, and fired at 900 to 1,600 F.

Selenium pigments may be used in printing inks. Such an ink is required on a poster or card where durability and brilliance are sought. Soap, containing alkali, would require a red printing ink containing selenium for its printed wrapper.

During this study the major compounders of pigments were contacted and pertinent information was obtained concerning the quantity of selenium used, the processing methods, and the type of air pollution control equipment in service. Emission records were not available, but estimates averaged 15 pounds selenium emissions per ton of selenium processed. All reported that bag filters are used for emission control.

The selenium emissions to the atmosphere during 1969 totaled 1,500 pounds.

Miscellaneous - Of the 728 tons of selenium consumed in the United States during 1969 about 125 tons were used in pharmaceutical products, blasting caps, rubber goods, steel alloys, and various other miscellaneous applications. It is used in a variety of metallurgical processes. Its use as iron selenide or ferroselenium is of some importance and addition of selenium to stainless steels is most common. It is employed to improve casting, forging, and machinability. The selenium content of casting steel alloys ranges from 0.01 to 0.05 percent, forging steels from 0.18 to 0.22 percent, and free-machining steels from 0.05 to 0.35 percent.

Sodium selenate is added to chromium plating baths because

its presence permits the deposition of chromium in a form that gives the plating a superior ability to protect the basic metal against corrosion. Such chromium plating also has a dull luster with decreased glare, making it desirable for protective and decorative automobile parts. Additions of selenium to magnesium and magnesium alloys provides protection from corrosion by seawater. Copper and copper alloys containing some copper selenide have better machinability and working properties.

The rubber industry uses finely ground metallic selenium and Selenac with rubber to increase the vulcanization rate and improve the aging and mechanical properties of low-sulfur stocks.

Selenium and its compounds may be added to lubricating oils and greases. It helps as an oxidation inhibitor and the barium, calcium, and zinc salts of selenic acids improve the detergent qualities of lubricating oils.

Selenium dioxide serves as an important oxidizing agent and catalyst in the synthesis of organic chemical and drug products. It is used in manufacturing cortisone and niacin, as well as in a wide variety of organic reactions such as

oxidation, hydrogenation, condensation, cracking, halogenation, and polymer treatment.

Selenium sulfide is used in producing a fungicide to control dandruff and dermatitis. Selenium in certain forms is effective in preventing muscular dystrophy in animals, white muscle disease in sheep, and muscle inflammation in horses. It has been used to lessen pneumonia in lambs, prevent premature still-born calves, and prevent barrenness in ewes. In poultry it prevents exudative diathesis and in pigs, hepatosidietetica.

Selenium compounds are used in photography to produce prints with warm brown tones, and in the manufacture of supersensitive photographic dyes.

Sodium selenate is used to some extent in commercial greenhouses as an insecticide for carnations and chrysanthemums. It is transformed by the plants into volatile selenides which repel red spiders, mites, thrips, and aphids.

Delay-action blasting caps employ selenium as an oxidizing agent when added with lead in gasless ignition charges, and as a reducing agent when mixed with barium peroxide in gasless fuse powders.

Manufacturers' records of selenium emissions are not available; however, the Contractor's estimate of 1,250 pounds selenium emissions during 1969 has been prepared assuming the average loss to be 10 pounds per ton of selenium processed.

OTHER SOURCES OF SELENIUM EMISSIONS

COAL

A search has been conducted and a limited amount of information has been found regarding the selenium content of coal. Some data was recorded in the literature; however, the most recent was that obtained from the Environmental Protection Agency, Office of Air Programs. During 1971 several coal samples were analyzed for the EPA using the neutron activation method to determine concentrations of several elements, including selenium. The average selenium content of 15 samples of coal from various parts of the United States was about 8 ppm.

During the combustion of coal, selenium is discharged with the ash: part with the bottom ash and part with the fly ash. The fly ash averages about 65 percent of the total ash.

Calculations have been made based on:

- (a) 516,084,000 tons of bituminous and anthracite coal consumed in the United States during 1969¹
- (b) an average selenium content of 8 ppm

1- Minerals Yearbook Bureau of Mines 1969.

- (c) fly ash 65 percent of total ash;
- (d) 85 percent average efficiency of control; and
- (e) 90 percent application of control.

The selenium emissions calculated by this method total 630 tons.

$$516,084,000 \times 8 \times 10^{-6} \times 0.65 [1 - (0.85 \times 0.90)] = 630$$

OIL

Until recently data concerning the selenium content of crude and residual oils was virtually nonexistent. However, during 1971 several foreign and domestic oil samples were analyzed for the Environmental Protection Agency, Office of Air Programs, using neutron activation analysis to determine metal concentrations. The average selenium content of 10 samples of foreign and domestic crude oil was 0.4 ppm. The average for 27 samples of imported residual oil was 0.6 ppm.

The residual fuel oil used in the United States during 1969, exclusive of use in vessels, was 639 million barrels. This oil containing selenium at an estimated 0.6 ppm (average) was used by industrials, electric utility companies, railroads, oil companies, and the military, as well as for heating (Tables VI and VII).

TABLE VI
RESIDUAL FUEL OIL DATA

Residual Oil Burned - 1969 (bbls)	639,048,000
Pounds per Barrel	340
Selenium Content of Oil (ppm)	0.6

Based on the data in Table VI, the selenium emissions to the atmosphere due to combustion of residual oil totaled 65 tons during 1969.

TABLE VII
SHIPMENTS OF RESIDUAL FUEL OIL
IN THE UNITED STATES - 1969

<u>Use</u>		<u>Million Barrels</u>
Heating		178.1
Industrial		170.3
Electric Utilities		247.6
Military and Other		<u>43.0</u>
TOTAL		639.0
<u>States</u>		
Northeast		367.7
New York	121.2	
Massachusetts	73.0	
New Jersey	68.8	
Pennsylvania	52.5	
Connecticut	29.3	
Other	22.9	
South		120.9
Florida	42.5	
Virginia	22.0	
Other	56.4	
Pacific-Mountain		89.7
California	53.5	
Washington	9.5	
Other	26.7	
North Central		60.7
Illinois	25.2	
Indiana	9.3	
Other	26.2	
TOTAL		<u>639.0</u>

"Shipments of Fuel Oil & Kerosine in 1970": Mineral Industry
Surveys: U. S. Dept. of the Interior Bureau of Mines:
Oct. 1, 1971.

IRON AND STEEL

During this study a search was made for data related to the quantity of selenium in raw materials used in the production of iron and steel, as well as the composition of emissions from blast furnaces, electric furnaces, cupolas, and other equipment. There was nothing available showing selenium content, but there was information on several metals, including copper, which is closely associated with selenium.

Based on the data obtained concerning copper, the selenium emissions due to the production of iron and steel have been roughly estimated at less than one ton per year.

OTHER

Many likely sources of selenium emissions have been investigated, but information for emission estimates has not been available. Such sources include incineration, pulp and paper manufacture, sulfuric acid production, and other facilities where sulfur is used or is contained in the raw materials that are processed.

In Russia the main sources currently used for selenium recovery are the anode slimes of electrolytic copper and nickel refineries. Ranking next in importance are the sludges of gas-washing equipment of the sulfuric acid and the pulp and paper industries. Selenium is obtained by roasting selenium-bearing pyrite concentrates or by burning metallurgical sulfur.

The only information obtained from industry regarding miscellaneous emission sources was a small quantity of selenium reported in the effluent water from a zinc smelter.

INCINERATION

Reports from 2 sources contain some information regarding selenium emissions to the atmosphere that result from the incineration of solid waste. One report states that household, commercial, and municipal wastes are more than 250 million tons per year, and that approximately 8 percent of all municipal solid waste is burned in municipal incinerators 1/.

The other report shows the results of a 3-day incinerator study for the determination of selenium. Each day about 245 tons of municipal solid waste was burned. Tests the first day showed that stack emissions ranged from 33.7 to 62.6 pounds of selenium per million tons of refuse burned, with an average of 45 pounds per million tons. The second day the average was 15.9 pounds per million tons and the range was 8.9 to 22.8. The third day no selenium emissions were detected 2/.

1- Black, R. J., Muhich, A. T., Klee, A. J., Hickman, H. L. Jr., and Vaughn, R. D. "The National Solid Wastes Survey, an Interim Report". (Presented at the 1968 Annual Meeting of the Institute of Solid Wastes of the American Public Works Association, Miami Beach, Florida, Oct. 24, 1968.)

2- Johnson, Henry: "Determination of Selenium in Solid Waste"; Environ. Sci. Technol., 4 (10) 850-853, Oct., 1970.

The incinerator tests to determine selenium emissions were limited in number and may not truly represent a nation-wide average; however, these test figures are the only such data currently available. If we assume the national average emission factor to be 20 pounds of selenium per million tons of refuse burned, then emissions in the United States are about 400 pounds per year.

UPDATING OF EMISSION ESTIMATES

The emissions and emission factors presented in this report are the result of calculations based principally on information obtained from industrial sources. They are specifically for the year 1969, but may be updated at any time when additional information is available. Either of the 2 methods described herein may be used for updating; however, the longer procedure, referred to as Method A, will yield results that are much more reliable.

The procedures to be followed with Method A are essentially the same as those used during the original study, which are described briefly as follows. More than 100 inquiries were sent to processing and reprocessing companies by mail or delivered during personal visits to plant sites. Some refused to furnish information and others stated it was not readily available. However, there were 52 companies that furnished all or part of the data requested and this was used as the basis for emissions and emission factors set forth in this report.

All of the companies that produce primary selenium were requested to provide the essential data required for the study. Some information was obtained from 2 of the 5 producers.

The reprocessing companies that provided information represented about 30 percent of the industry capacity.

Regardless of the method selected, the first step to be taken when updating the emission estimates is to obtain the latest issue of the Bureau of Mines Minerals Yearbook, Volume I-II, which is normally available within 16 or 18 months after the end of the calendar year (preprints of individual sections are usually available sooner). This publication shows the quantity of selenium produced in the United States, as well as the quantity imported. Additional information may be obtained from the Bureau of Mines concerning the amount of selenium consumed and the various purposes for which it is used, and otherwise supplement the information shown in the Minerals Yearbook. All of the information required to update the material flow chart for selenium is available from these 2 sources.

When using Method A the emission factors must be revised by contacting industry to determine the improvements in air pollution collection equipment efficiency and other factors affecting selenium emissions. The revised emission factors may then be used with the production quantities obtained from the Minerals Yearbook or other referenced sources.

Method B is considerably shorter than Method A and less reliable. The only requirement is to revise the material flow chart according to the most recent data available from the Bureau of Mines and apply the emission factors shown in this report. This method is only a partial updating since there is no determination regarding improvements in air pollution control or any other considerations affecting emission factors.

To update selenium emissions from metallurgical processing and the glass industry, it is preferable to use Method A. The remaining emissions shown in this report may be updated by using Method B without introducing an appreciable error into the results.